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TITLE: Coating compsn - contg copolymer of vinylacetate ethylene and vinyl ester of carboxylic acid

PATENT-ASSIGNEE: NIPPON SYNTHETIC CHEM IND CO[NISY]

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BASIC-ABSTRACT: A coating compsn. which contains an aq. emulsion of a copolymer ³⁵⁻⁷⁰ ₁₀₋₄₀ consisting of 10-85 pt.wt. of vinyl acetate, 10-60 pts. wt. of ethylene and 5-30 pt. wt. of vinyl ester of tert. aliphatic carboxylic acid as the main agent.

¹⁰⁻⁴⁵ Coating have good flexibility, weather, resistance, adhesion etc. ^{10 or more} _{20 or more}

TITLE-TERMS:

COATING COMPOSITION CONTAIN COPOLYMER ETHYLENE VINYL ESTER CARBOXYLIC ACID

DERWENT-CLASS: A14 A17 A82 G02

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⑩被覆用組成物

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発明の詳細な説明

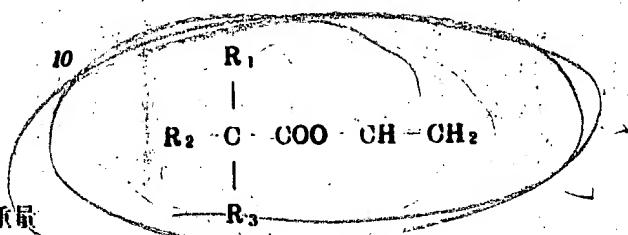
本発明は、酢酸ビニル成分10～85部(重量部、以下同様)、エチレン成分10～60部および第3級脂肪族カルボン酸のビニルエステル成分5～30部からなる共重合物の水性エマルジョンを主剤としてなる被覆用組成物にかかるものである。

ポリ酢酸ビニルエマルジョンは塗料用として広く用いられているが、その乾燥皮膜は一般に耐水性、耐アルカリ性が充分でなく、また弾力性や柔軟性にも欠けるという難点がある。したがつて従来は弾力性や柔軟性を改善するためにジブチルフタレート、ジオクチルフタレートなどのとき可塑剤を配合する方法が行なわれているが、かかる方法によるときは弾力性や柔軟性は向上せしめるが、ポリ酢酸ビニルエマルジョンから製した皮膜の欠点である耐水性および耐アルカリ性は改善されないばかりかかえつて低下し、かつ耐候性もいちじるしく悪化するという問題を生ずる。

しかるに本発明者らは鋭意研究を重ねた結果、酢酸ビニルにエチレンおよび第3級脂肪族カルボン酸のビニルエステルを前記特定の割合で共重合せしめてえた水性エマルジョンは、ポリ酢酸ビニルエマルジョンが本来有する下地に対する密着性、皮膜の耐候性、堅牢性などの諸性質をほとんど損なうことなく、その皮膜の弾力性および柔軟性を

いちじるしく改善しると共に耐水性、耐アルカリ性をも顕著に向上せしめうるのであつて、ポリ酢酸ビニルエマルジョンを使用するばあいの前記のごとき問題点をいずれもほぼ完全に解消せしめるといううまつたく新たな事実を見出し、本発明を完成するにいたつた。

前記第3級脂肪族カルボン酸のビニルエステルは、一般式



で表わされる化合物で、そのR₁、R₂およびR₃で示されるアルキル基の炭素数の合計は3～11程度とすることが望ましい。かかるビニルエステルを例示すれば、たとえばトリメチル酢酸ビニル、ネオペンタノン酸ビニル、ネオヘキサノン酸ビニル、ネオヘプタノン酸ビニル、ネオオクタノン酸ビニル、ネオノナノン酸ビニル、ネオデカノン酸ビニル、ネオウンデカノン酸ビニル、ネオドデカノン酸ビニル、ネオトリデカノン酸ビニルなどが好適なものとしてあげられる。これらは単独あるいは2種以上を併用して用いてもよい。

本発明の被覆用組成物における共重合物は、酢酸ビニル成分10～85部、エチレン成分10～60部および第3級脂肪族カルボン酸のビニルエステル成分5～30部からなることを必須とするものであつて、第3級脂肪族カルボン酸のビニルエステル成分の割合を5%以下の少量とするときは耐水性、耐アルカリ性を充分に改善することができずしかも皮膜は表面粘着が高くなるという欠点が生じる。一方30%以上の多量にするときは下地に対する密着性の低下の問題が生じる。またエチレン成分の割合を10%以下とするときは弾性が低下し酢酸ビニル重合物のかたくてもろい

3-11

性質が顕著にあらわれ、また耐水性、耐アルカリ性も低下するので不適当であり、一方60%以上とするときは、エチレンの結晶性があらわれてポリマーの弾性を失なうとともに、下地に対する密着性および低温造膜性が低下するなど全般的に塗膜物性が低下するという難点がある。

これら共重合物エマルジョンの製造法としてはとくに制限はなく、通常のビニルエステルとの乳化重合方法に準じて反応せしめればよい。たとえば乳化剤、保護コロイド剤などを溶解した水溶液にエチレン、酢酸ビニルおよび第3級脂肪族カルボン酸のビニルエステルを加え、乳化重合触媒の存在下にエチレン圧10~150気圧程度、温度20~80°C程度で重合反応を行なわせることにより目的とする共重合物エマルジョンがえられる。

しかして該共重合物のエマルジョンは適宜顔料、分散剤、消泡剤、増粘剤、凍結安定剤などが配合され、金属性、コンクリート、木材、紙、合成樹脂などの被覆剤として広く一般に適用されうる。

つぎに実例をあげて、本発明の被覆用組成物を説明する。なお例中において部とあるのは重量部である。

例 1

ドデシルベンゼンスルホン酸ソーダ2部およびポリエチレンオキサイドノニルフェニールエーテル4部を溶解した水300部に、酢酸ビニル240部およびネオデカノン酸ビニル70部を加えて乳化せしめ、これに過硫酸カリウム(重合触媒)2.5部を添加し、ついでエチレンを圧入しな

がら圧力40気圧、温度65°Cの条件下で10時間乳化重合反応を行なつた。その結果、樹脂分濃度50%、酢酸ビニルとエチレンとネオデカノン酸ビニルの共重合比が重量でそれぞれ5.5:3.0:1.5の共重合物の水性エマルジョンをえた。このエマルジョンを用いて、つぎの処方にしたがい塗料を調製した。

| | |
|------------------|---------|
| 前記水性エマルジョン | 42.5 部 |
| 酸化チタン(白色顔料) | 23.0 " |
| クレー(体质顔料) | 6.0 " |
| タルク(体质顔料) | 1.0.0 " |
| ヘキサメタ矯酸ソーダ10%水溶液 | 2.3 " |
| トリプチルホスフェート | 0.05 " |
| メチルセルロース2%水溶液 | 1.0.0 " |
| 水 | 3.6 " |
| エチレングリコール | 3.5 " |

えられた塗料をフレキシブルボード上に刷毛を用いて2回塗りを行ない、該塗料の性能を試験した。

なお対照例として、水性エマルジョンの共重合組成を第1表に示すとく変更したほかは例1と同様に操作してえた塗料についても実験を行なつた。

これらの実験結果を第1表に示す。

第一表

| 例番号 | 例1 | 対照例1 | 対照例2 | 対照例3 | 対照例4 | 対照例5 |
|---------|------------|---------|--------|---------|------------|---------|
| 共重合物組成部 | エチレン | 30 | - | 7 | 65 | 30 |
| | 酢酸ビニル | 55 | 100 | 78 | 25 | 70 |
| | ネオデカノン酸ビニル | 15 | - | 15 | 10 | 3 |
| 塗工性 | 刷毛サバキ | ◎ | △ | ○ | ○ | ○ |
| | 調色性 | ◎ | ○ | ○ | ○ | ○ |
| | タッチアップ | ◎ | ○ | ○ | ○ | ○ |
| | 刷毛ムラ | ◎ | ○ | ○ | ○ | ○ |
| | レベリング | ◎ | ○ | ○ | ○ | ○ |
| 塗膜性能 | 光沢 | ◎ | ○ | ○ | △ | ○ |
| | 密着性 | 100/100 | 90/100 | 100/100 | 60/100 | 100/100 |
| | 耐水性 | ◎ | △(軟化) | △(軟化) | △(ブリスター発生) | ○ |
| | 耐アルカリ性 | ◎ | × | × | ○ | △ |
| | 耐洗浄性 | >1000 | 250 | 450 | 300 | 650 |
| 耐候性 | 耐候性 | 5 | 1 | 2 | 3 | 2 |
| | 粘着性 | ◎ | ○ | (○) | ○ | △ |

(対照例1においては、さらにジブチルフタレート(可塑剤)15部を配合した)

注 1 刷毛サバキは、刷毛のノビがよく、刷毛の抵抗のほとんどないものを◎とし、順次○、△、×にてランク別けした。

2 調色性は、色票B-13-740を基準とし、基準とはほとんど同一の色調を示すものを◎とし、順次○、△、×にてランク別けした。

3 タッチアップは、塗工後24時間放置し、ついで塗り重ねを行ない、塗り重ね部分の下地との識別のほとんどつけ難いものを◎とし、順次○、△、×にてランク別けした。

4 刷毛ムラは、刷毛塗り時およびえらびえられた乾燥塗膜について刷毛ムラの認められないものを◎とし、順次○、△、×にてランク別けした。

5 レベリングは、乾燥塗膜のハケ目について凹凸の状態を観察し、ほとんど認められないものを◎とし、順次○、△、×にてランク別けした。

6 光沢は、塗膜の60-60°反射光の光沢について目視判定を行なつた。
非常に良好なものを◎とし、順次○、△、×にてランク別けした。

7 密着性は、塗膜の表面に2番目のゴバン目を100個つくり、ついでその上にセロテープを一旦貼りつけてはがし、100個のゴバン目のうち下地に密着しているものの数で示した。

8 耐水性は、既消しフタル酸エナメル塗りガラス板の上に塗工し、風乾したのち、温度20℃の水中に18時間浸漬し、塗膜の変化を観察した。塗膜の軟化、変色、ブリスターの発生がまったく認められないものを◎とし、順次○、△、×にてランク別けした。

9 耐アルカリ性は、試料を温度20℃の水酸化カルシウム飽和水溶液中に18時間浸漬し、

塗膜の変化を観察した。塗膜の軟化、変色、ブリスターの発生のはとんど認められないものを◎とし、順次△、△、×にてランク別けした。

10 耐洗浄性は疎消しタル酸・ナメル塗りガラス板の上に塗上し、風乾した塗膜をウォッシュアビリティテスター (Wash ability tester) にかけ、下地のあらわれるまでの摩擦の回数で示した。

11 耐候性は、ウエザーオメーターにより1000時間照射したのちの変化を観察し、変色、白化などの変化のはとんど認められないものを5とし、順次4, 3, 2, 1にてランク別けした。

12 粘着性は、塗膜の上にガーゼを5枚重ね、ガーゼの中央に径40mm、重層500gで底面の平らな円柱形のオゼリをのせ、温度35±1°Cで18時間放置し、粘着の程度を観察した。粘着のはとんど認められないものを◎とし、順次△、△、×にてランク別けした。

例 2~6

*を種々変更したほかは例1と同様にしてえた塗料

例1における共重合物エマルジョンの共重合比* の性能を試験した。その結果を第2表に示す。

第 2 表

| 例 番 号 | | 2 | 3 | 4 | 5 | 6 |
|---------|------------|---------|--------|---------|--------|--------|
| 共重合物組成部 | エチレン | 15 | 45 | 15 | 15 | 45 |
| | 酢酸ビニル | 70 | 45 | 77 | 60 | 30 |
| | ネオデカノン酸ビニル | 15 | 10 | 8 | 25 | 25 |
| 塗工性 | 刷毛サバキ | ○ | ○ | ○ | ○ | ○ |
| | 調色性 | ○ | ○ | ○ | ○ | ○ |
| | タツチアップ | ○ | ○ | ○ | ○ | ○ |
| | 刷毛ムラ | ○ | ○ | ○ | ○ | ○ |
| | レベリング | ○ | ○ | ○ | ○ | ○ |
| 塗膜性能 | 光沢 | ○ | ○ | ○ | ○ | ○ |
| | 密着性 | 100/100 | 90/100 | 100/100 | 95/100 | 85/100 |
| | 耐水性 | ○ | ○ | ○ | ○ | ○ |
| | 耐アルカリ性 | ○ | ○ | ○ | ○ | ○ |
| | 耐洗浄性 | 1000 | >1000 | 950 | >1000 | >1000 |
| | 耐候性 | 4 | 5 | 4 | 5 | 5 |
| 粘着性 | 粘着性 | ◎ | ○ | ○ | ○ | ○ |

例 7~9

例1におけるネオデカノン酸ビニルに代えて、2-2-ジメチルパレリン酸ビニル(例7)、ネオトリデカノン酸ビニル(例6)およびトリメチル酢酸ビニル(例9)を用いた他は例1と同様に45ルを用いた例(対照例7)についても例7と同様

して実験を行なつた。

なお対照例として例7における2-2-ジメチルパレリン酸ビニルの代りにステアリン酸ビニルを用いた例(対照例6)、n-パレリアン酸ビニ

にして実験を行なつた。

実験結果を第3級表に示す。

第 3 表

| 例 番 号 | 例 7 | 例 8 | 例 9 | 対照例 6 | 対照例 7 |
|-----------|---|----------------------------|--------------------------|-------------------------|---------------------------|
| 共重合物組成(部) | ビニルエステル (2-2-ジメチル バレリン 酸ビニル) 15 | ネオトリ デカノン 酸ビニル 15 | トリメチ ル酢酸ビ ニル 15 | ステアリ ン酸ビニ ル 15 | ノーバレ リアン酸 ビニル 15 |
| | エチレン 15 | 15 | 15 | 15 | 15 |
| | 酢酸ビニル 70 | 70 | 70 | 70 | 70 |
| 塗工性 | 刷毛サバキ | ◎ | ◎ | ◎ | ◎ |
| | 調色性 | ◎ | ◎ | ◎ | ◎ |
| | タッチアップ | ◎ | ◎ | ◎ | ◎ |
| | 樹毛ムラ | ◎ | ◎ | ◎ | ◎ |
| | レベリング | ◎ | ◎ | ◎ | ◎ |
| 塗膜性能 | 光沢 | ◎ | ◎ | ◎ | ◎ |
| | 密着性 | 100/100 | 95/100 | 100/100 | 85/100 |
| | 耐水性 | ◎ | ◎ | ◎ | ○ |
| | 耐アルカリ性 | ◎ | ◎ | ◎ | ○ |
| | 耐洗浄性 | >1000 | >1000 | 980 | 650 |
| | 耐候性 | 5 | 5 | 5 | 3 |
| | 粘着性 | ◎ | ◎ | ○ | △ |

特許請求の範囲

1 酢酸ビニル成分 10~85 重量部、エチレン
成分 10~60 重量部および第3級脂肪族カルボ

30 ン酸のビニルエステル 5~30 重量部からなる共
重合物の水性エマルジョンを主剤としてなる被覆
組成物。

PTO 03-3811

Japanese Patent

Document No. Sho 47-3705

COATING COMPOSITION

[Hifuku Yo Soseibutsu]

Kano Fukushima and Tadashi Ishibashi

UNITED STATES PATENT AND TRADEMARK OFFICE

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Detailed explanation of the invention

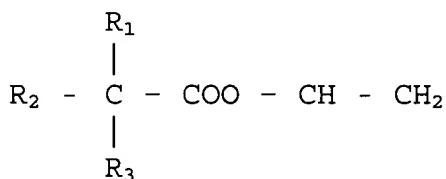
The present invention pertains to a coating composition having an aqueous emulsion of a copolymerized product as a main agent composed of 10-85 parts (parts by weight, hereinafter, the same) vinyl acetate component, 10-60 parts ethylene component, and 5-30 parts vinyl ester component of a tertiary aliphatic carboxylic acid.

The polyvinyl acetate emulsion is broadly used as a paint, however its dry coated film generally has insufficient water resistance and alkali resistance and is also deficient in elasticity and flexibility. Therefore, in order to improve the elasticity and the flexibility, plasticizers such as dibutyl phthalate and dioctyl phthalate have been mixed. In such a method, though the elasticity and the flexibility are improved, the water resistance and the alkali resistance, which are drawbacks of coated films made of the polyvinyl acetate emulsion, are not only not improved but are lowered, and the weather resistance is also considerably deteriorated.

¹ Numbers in the margin indicate pagination in the foreign text.

Thus, these inventors repeatedly researched the above problems in earnest. As a result, it was newly discovered that an aqueous emulsion obtained by copolymerizing vinyl acetate with ethylene and vinyl ester of a tertiary aliphatic carboxylic acid at the above-mentioned specific ratio could markedly improve the elasticity and flexibility of its coated film with little damaging the properties such as adhesion to the original substrate of the polyvinyl acetate and durability, could considerably improve the water resistance and the alkali resistance, and could almost completely solve the above-mentioned problems of the polyvinyl acetate emulsion. Then, the present invention was completed.

The vinyl acetate of the above-mentioned tertiary aliphatic carboxylic acid is a compound represented by the following general formula.



The total of carbons of the alkyl group represented by these R_1 , R_2 , and R_3 is preferably about 3-11. As the vinyl ester, for example, vinyl trimethylacetate, vinyl neopentanoate, vinyl neohexanoate, vinyl neoheptanoate, vinyl neoctanoate, vinyl neononanoate vinyl neodecanoate, vinyl neoundecanoate, vinyl

neodoecanoate, vinyl neotridecanoate, etc., are appropriately mentioned. They may be used alone or in combination of two kinds or more.

The copolymerized product in the coating composition of the present invention is essentially composed of 10-85 parts vinyl acetate component, 10-60 parts ethylene component, and 5-30 parts vinyl ester component of a tertiary aliphatic carboxylic acid. When the ratio of the vinyl ester component of the tertiary aliphatic carboxylic acid is a small amount of 5% or less, the water resistance and the alkali resistance cannot be sufficiently improved, and the surface adhesion is raised in its coated film. On the other hand, if the ratio is a large amount of 30% or more, the adhesion to the substrate is lowered. Also, when the ratio of the ethylene component is 10% or less, the elasticity is lowered, and a hard and brittle property of the vinyl acetate polymerized product appears distinctly. Also, /2 the water resistance and the alkali resistance are lowered, which is inappropriate. On the other hand, when the ratio is 60% or more, the crystallinity of the ethylene appears, so that the elasticity of the polymer is lost and the adhesion to the substrate and the low-temperature film formability is lowered. As a result, the entire coated film properties are lowered.

The method for manufacturing this copolymerized emulsion is not particularly limited, and the reaction may be carried out according to an emulsion polymerization method with an ordinary vinyl ester. A vinyl acetate and a vinyl ester of a tertiary aliphatic carboxylic acid are added to an aqueous solution in which protective colloidal agent, etc., are dissolved, subjected to a polymerization reaction at an ethylene pressure of about 10-150 atm and a temperature of about 20-80°C in the presence of an emulsion polymerization catalyst, so that an intended copolymerized emulsion can be obtained.

Then, the emulsion of said copolymerized product is mixed with appropriate pigments, dispersants, defoaming agents, tackifiers, freezing stabilizers, etc., and can be generally broadly applied as a coating agent of metals, concretes, woods, papers, synthetic resins, etc.

Next, the coating composition of the present invention is explained by application examples. Also, part in the examples means part by weight.

Example 1

240 parts vinyl acetate and 70 parts vinyl neodecanoate were added to 300 parts water in which 2 parts soda dodecylbenzenesulfonate and 4 parts polyethylene oxide nonylphenyl ether and emulsified, and 2.5 parts potassium

persulfate (polymerization catalyst) was added to it. Then, while press-feeding ethylene, its emulsion polymerization reaction was carried out for 10 h under the conditions of a pressure of 40 atm and a temperature of 65°C. As a result, an aqueous emulsion of a copolymerized product with a resin portion concentration of 50% and a copolymerization ration of vinyl acetate, ethylene, and vinyl neodecanoate of 55:30:15 was obtained. Using the emulsion, a paint was prepared according to the following prescription.

| | |
|--|------------|
| Said aqueous emulsion | 42.5 parts |
| Titanium oxide (white pigment) | 23.0 parts |
| Clay (extender) | 6.0 parts |
| Talc (extender) | 10.0 parts |
| 10% aqueous solution of soda hexametaphosphate | 2.3 parts |
| Tributyl phosphate | 0.05 part |
| 2% aqueous solution of methyl cellulose | 10.0 parts |
| Ethylene glycol | 3.5 parts |

The paint obtained was applied twice on a flexible board by a brush, and the performances of said paint were tested.

Also, as a comparative example, a paint obtained by operating similarly to Example 1 except for changing the copolymerization composition of the aqueous emulsion as shown in Table I was also experimented.

These experimental results are shown in Table I.

Table I

/3

| Example No. | | Example 1 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 | Comparative Example 5 |
|--|---|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Copolymerized product composition (part) | Ethylene Vinyl acetate Vinyl neodecanoate <i>Neova</i> | 30 55 15 | - 100 - | 7 78 15 | 65 25 10 | 30 70 - | 15 82 3 |
| Paint performances | Brush Handling Toning characteristic Touch-up Brush irregularity Leveling | ◎ ◎ ◎ ◎ ◎ | Δ ○ ○ ○ ○ | ○ ○ ◎ ○ ◎ | ○ ○ ○ ○ ○ | ○ ◎ ◎ ◎ ◎ | ○ ◎ ◎ ◎ ◎ |

| | | | | | | | |
|--|-----------------------|---------|------------------|------------------|---------------------------------|---------|---------|
| Coated film perfor man ces | Gloss | ◎ | ○ | ○ | △ | ○ | ○ |
| | Adhesion | 100/100 | 90/100 | 100/100 | 60/100 | 100/100 | 100/100 |
| | Water resistance | ◎ | △(sof tening) | △(sof tening) | △(bli ster gener ated) | ○ | ○ |
| | Alkali resistance | ◎ | X | X | ○ | △ | △ |
| | Washing resistance | >1000 | 250 | 450 | 300 | 650 | 560 |
| | Weather resistance | 5 | 1 | 2 | 3 | 3 | 2 |
| | Tackiness | ◎ | ◎ | ○ | ○ | △ | ○ |

(In Comparative Example 1, 15 parts dibutyl phthalate (plasticizer) was further mixed.)

Notes:

1. In the brush handling, when the extension of the brush was good and the resistance of the brush was little, it was assumed as ◎. Then, ○, △, and X were sequentially ranked.
2. In the toning characteristic, assuming the color mark No. B-13-740 as a standard, when almost the same hue as the standard, it was assumed as ◎. Then, ○, △, and X were sequentially ranked.

3. In the touch-up, after paining and holding for 24 h, paining was reapplied, and when the identification of the substrate of the repainted part was almost difficult, it was assumed as ◎. Then, O, Δ, and X were sequentially ranked.

5. In the leveling, the concave and convex state of the brush meshes of the dry coated film were observed, and when the state was seldom recognized, it was assumed as ◎. Then, O, Δ, and X were sequentially ranked.

6. In the gloss, the gloss of 60-60° reflected lights of the coated film was judged with the naked eyes.

7. In the adhesion, 100 pieces of grids of 2 mm were formed on the surface of the coated film, and a cellophane tape was once attached onto it and peeled off. The number of grips attached to the substrate among 100 pieces of grids was shown.

8. In the water resistance, after painting the composition on a delusted enamel phthalate-coated glass plate, it was dried with the air and immersed for 18 h into water at a temperature of 20°C, and the change of the coated film was observed. When softening, discoloration, and blister generation of the coated film were not recognized at all, it was assumed as ◎. Then, O, Δ, and X were sequentially ranked.

9. In the alkali resistance, the sample was immersed for 18 h into a calcium hydroxide-saturated aqueous solution at a

temperature of 20°C, the change of the coated film was /4
observed. When softening, discoloration, and blister generation
of the coated film were seldom recognized, it was assumed as 0.
Then, O, Δ, and X were sequentially ranked.

10. In the washing resistance, after the composition was painted
on the enamel phthalate-coated glass plate and dried with the
air, the coated film was subjected to a wash ability tester.
The abrasion times until the appearance of the substrate was
shown.

11. In the weather resistance, after irradiating for 1000 h by a
wetherometer, the change was observed, and when the changes such
as discoloration and whitening were seldom recognized, it was
assumed as 5. Then, 4, 3, 2, and 1 were sequentially ranked.

11. In the tackiness, 5 sheets of gauzes were overlapped on the
coated film, and a columnar weight with a flat bottom face, a
diameter of 40 mm, and a weight of 500 g was put at the center
of the gauzes and held at $35 \pm 1^\circ\text{C}$ for 18 h. The degree of
tackiness was observed. When the tackiness was seldom
recognized, it was assumed as (. Then, O, Δ, and X were
sequentially ranked.

Examples 2-6

The performances of paints obtained similarly to Example 1
except for variously changing the copolymerization ratio of the

copolymerized product emulsion in Example 1 were tested. The results are shown in Table II.

Table II

| Example No. | | 2 | 3 | 4 | 5 | 6 |
|--|-----------------------|----|----|----|----|----|
| Copolymerized product composition (part) | Ethylene | 15 | 45 | 15 | 15 | 45 |
| | Vinyl acetate | 70 | 45 | 77 | 60 | 30 |
| | Vinyl neodecanoate | 15 | 10 | 8 | 25 | 25 |
| Paint performances | Brush Handling | ○ | ○ | ○ | ○ | ○ |
| | Toning characteristic | ○ | ○ | ○ | ○ | ○ |
| | Touch-up | ○ | ○ | ○ | ○ | ○ |
| | Brush irregularity | ○ | ○ | ○ | ○ | ○ |
| | Leveling | ○ | ○ | ○ | ○ | ○ |

| | | | | | | |
|--|-----------------------|---------|--------|---------|--------|--------|
| Coated film perfor man ces | Gloss | ○ | ◎ | ○ | ◎ | ◎ |
| | Adhesion | 100/100 | 90/100 | 100/100 | 95/100 | 85/100 |
| | Water resistance | ○ | ◎ | ○ | ◎ | ○ |
| | Alkali resistance | ○ | ◎ | ○ | ◎ | ◎ |
| | Washing resistance | >1000 | >1000 | 950 | >1000 | >1000 |
| | Weather resistance | 4 | 5 | 4 | 5 | 5 |
| | Tackiness | ◎ | ○ | ◎ | ◎ | ◎ |

Examples 7-9

Experiments were carried out similarly to Example 1 except for using vinyl 2,2-dimethylvalerate (Example 7), vinyl neotridecanoate (Example 6), and vinyl trimethylacetate (Example 9) instead of the vinyl neodecanoate in Example 1.

Also, as comparative examples, an example (Comparative Example 6) using vinyl stearate instead of the vinyl 2,2-dimethylvalerate in Example 7 and an example (Comparative Example 7) using vinyl n-valerianate were experimented similarly to Example 7. The experimental results are shown in Table /5

III.

Table II

| Example No. | | Example 7 | Example 8 | Example 9 | Comparative Example 6 | Comparative Example 7 |
|--|-----------------------|------------------------------------|--------------------------------|--------------------------------|------------------------|-----------------------------|
| Copolymerized product composition (part) | Vinyl ester | (Vinyl 2,2-dimethylvalerate) 15 | (Vinyl neotri-decanoate) 15 | (Vinyl trimethylacetate) 15 | (Vinyl stearate) 15 | (Vinyl n-valerianate) 15 |
| | Ethylene | 15 | 15 | 15 | 15 | 15 |
| | Vinyl acetate | 70 | 70 | 70 | 70 | 70 |
| Paint performances | Brush Handling | ◎ | ◎ | ◎ | ◎ | ◎ |
| | Toning characteristic | ◎ | ◎ | ◎ | ◎ | ◎ |
| | Touch-up | ◎ | ◎ | ◎ | ◎ | ◎ |
| | Brush irregularity | ◎ | ◎ | ◎ | ◎ | ◎ |
| | Leveling | ◎ | ◎ | ◎ | ◎ | ◎ |

| | | | | | | |
|--|-----------------------|---------|--------|---------|--------|--------|
| Coated film perfor man ces | Gloss | ◎ | ◎ | ◎ | ◎ | ◎ |
| | Adhesion | 100/100 | 95/100 | 100/100 | 85/100 | 90/100 |
| | Water resistance | ◎ | ◎ | ◎ | ○ | ○ |
| | Alkali resistance | ◎ | ◎ | ◎ | ○ | ○ |
| | Washing resistance | >1000 | >1000 | 980 | 650 | 700 |
| | Weather resistance | 5 | 5 | 5 | 3 | 3 |
| | Tackiness | ◎ | ◎ | ○ | △ | △ |

Claim

1. A coating composition, characterized by having an aqueous emulsion of a copolymerized product as a main agent composed of a vinyl acetate component at 10-85 parts by weight, an ethylene component at 10-60 parts by weight, and a vinyl ester component of a tertiary aliphatic carboxylic acid at 5-30 parts by weight.